MASTER COPY   KEEP THIS COPY FOR REPRODUCTION PURPOSES

REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

1. AGENCY USE ONLY (*Leave blank*)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	07/20/95	Final Report 05/01/92 - 04/30/95

4. TITLE AND SUBTITLE
Molecular Level Assemblies of Poly-pyridyl Complexes at Metal Oxide and Glass Interfaces

5. FUNDING NUMBERS
DAAL03-92-G-0198

6. AUTHOR(S)
Thomas J. Meyer

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Dr. T.J. Meyer
Department of Chemistry, Univ. of North Carolina
CB#3290, Venable Hall
Chapel Hill, North Carolina, 27599-3290

8. PERFORMING ORGANIZATION REPORT NUMBER
29538-CH

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

N/A

14. SUBJECT TERMS	15. NUMBER OF PAGES
Self Assembled Monolayers, Redox, Electrode, Ruthenium	9
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

FINAL REPORT

FORTY COPIES REQUIRED

1. ARO PROPOSAL NUMBER: 29538-CH

2. PERIOD COVERED BY REPORT: 1 May 1992 - 30 April 1995

3. TITLE OF PROPOSAL: Molecular Level Assemblies of Poly-pyridyl Complexes at Metal Oxide & Glass Interfaces

4. CONTRACT OR GRANT NUMBER: DAAL03-92-G-0198

5. NAME OF INSTITUTION: University of North Carolina at Chapel Hill

6. AUTHOR OF REPORT: Thomas J. Meyer

7. LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO SPONSORSHIP DURING THIS REPORTING PERIOD, INCLUDING JOURNAL REFERENCES:

"Molecular-Level, Electron Transfer and Excited State Assemblies on Surfaces of Metal Oxides and Glass." G.J. Meyer, B.W. Pfennig, J.R. Schoonover, C.J. Timpson, J.F. Wall, C. Kobusch, X. Chen, B.M. Peek, C.G. Wall, W. Oui, B.W. Erickson, C.A. Bignozzi, T.J. Meyer, Inorg. Chem., 1994, 33, 3952

"Binding and Reduction of Silver Ions in Thin Polymeric Films of Poly-[Fe(vbpy)$_2$(CN)$_2$],poly-vbpy." M. Bakir, S.G. MacKay, R.W. Linton, B.P. Sullivan, T.J. Meyer, Inorg. Chem., 1994, 33, 3945

"Synthesis of Redox Derivatives of Lysine and Glutamine for Solid-Phase Assembly of Light-Harvesting Peptides." D.G. McCafferty, B.M. Bishop, C.G. Wall, S.G. Hughes, S.L. Mecklenberg, T.J. Meyer, B.W. Erikson, Tetrahedron, 1995, 51, 1093

"Photophysics and Photochemistry of Chromophore-Quencher Assemblies on Glass and Powdered Silica." B.W. Pfennig, P. Chen, T.J. Meyer, Resubmitted to Inorg. Chem.

8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED DURING THIS REPORTING PERIOD:

Craig W. Wall (RA)	Ph.D. conferred
Cliff J. Timpson (RA)	Ph.D. conferred
Martin Devenney (Postdoc)	
Brian Pfennig (Postdoc)	

9. REPORT OF INVENTIONS (BY TITLE ONLY): N/A

Thomas J. Meyer
Department of Chemistry
Venable Hall, CB#3290
University of North Carolina at Chapel Hill
Chapel Hill, N.C. 27599-3290

Molecular Level Assemblies of Polypyridyl Complexes at Metal Oxide & Glass Interfaces

Final Report

Thomas J. Meyer

1 May 1992 - 30 April 1995

U.S. Army Research Office

Grant Number: DAAL03-92-G-0198

Department of Chemistry
University of North Carolina

Introduction

Much of the research effort of this group and others has been devoted to the study of the excited state properties and the redox chemistry of polypyridyl complexes of Ru^{II}, Os^{II} and Re^{I} transition metal ions in solution. As a consequence, well developed synthetic procedures exist for the preparation of a variety of these complexes and a wealth of information is available regarding the properties of this interesting class of molecules.

The crux of this research proposal was to carry out an in-depth study based on attaching these complexes to solid supports in an attempt to extend their versatility. The formation and characterization of structurally well defined arrays of redox or photoactive molecules on insulating or semiconductor substrates is an important element in the design of molecular-level devices. Any potential device applications however, had to be preceded by addressing the more fundamental questions of how to form stable monolayers of molecules at the solid support and, what effect would this constrained environment have on the fundamental photophysical and redox properties of the molecules.

Several groups had previously documented the immobilization of polypyridyl complexes on SnO_2 and TiO_2 surfaces based around $[Ru(bpy)_2(4,4'\text{-}(CO_2H)_2\text{-}bpy)]^{2+}$. The nature of the surface linkage was presumed to be ester formation between the bipyridine-COOH ligand and a surface metal-OH group. The work of Grätzel's group has recently demonstrated the important use of such interfaces. Regenerative photochemical cells with liquid junctions that have efficiencies approaching those of solid-state silicon devices have been manufactured. This was achieved via photosensitization of TiO_2 wide band gap semiconductor electrodes by immobilization of $Ru(4,4'\text{-}(CO_2H)_2\text{-}bpy)_2(CN)_2)$ at the metal oxide surface. The presence of the acid groups were shown to be important in "anchoring" the complex to the semiconductor which was in contact with the liquid electrolyte. The interaction between the acid groups and the TiO_2 was also thought to be important for efficient charge injection from the excited state of the bound chromophore into the conduction band of the semiconductor.

The starting point of our investigation was to determine protocols for the formation of stable monolayers of redox and photoactive molecules at various types of metal oxide supports. Insulating surfaces such as high surface area silica gel and glass (SiO_2) as well as semiconductor electrodes - Sn doped In_2O_3 (ITO), Sb doped SnO_2 (ATO) and powdered TiO_2 and SnO_2 were to be used as the metal oxide supports. A new area of direction that transpired during this proposal period was the immobilization of

ruthenium polypyridyl complexes in transparent silica sol-gel monoliths. This area evolved directly from the work on metal oxide supports and represents a highly versatile method for studying the interactions between the immobilized complexes and the SiO_2 surface. The common link between the insulating and conducting supports is the availability of surface oxo and hydroxyl groups through which it was proposed that the surface linkage chemistry would occur.

Much of the technical information that has resulted from this work has been included in interim reports submitted to the ARO and also in a detailed manuscript. (Meyer *et al* .Inorganic Chemistry, 1994, 33, 3952-3964)

Part 1: Formation of Redox and Photoactive Molecules on Metal Oxide Supports

A two-fold approach was utilized in forming stable monolayers of redox and photoactive molecules at metal oxide supports. One method was based on the self assembly of redox and photoactive molecules at the oxide interfaces. A requirement for such a process was that the molecule possess groups capable of chelating to the reactive surface groups on the metal oxide support. In the other approach, silyl functionalised semiconductor electrodes were fabricated. The polymerized silane monolayer contained reactive amino groups which could be further functionalised with redox active groups. The details regarding the immobilization of molecules in sol-gel matrices will be detailed in a later section.

(A) Self Assembled Monolayers on Surfaces

Much of the initial work revolved around the immobilization of carboxylic acid derivatives of phenothiazine (PTZ), ferrocene (Fc), viologen and polypyridyl complexes of Ru^{II}, Os^{II} and Re^{I}. Assemblies based on redox active amino acids and peptides containing ferrocene were also anchored to the surfaces. $[Ru(bpy)_2(4,4'\text{-}(CO_2H)_2\text{-}bpy)]^{2+}$ and related complexes were the most widely studied and were found to self assemble on to glass (SiO_2) and conductive metal oxide (SnO_2 and In_2O_3) surfaces. Both powdered semiconductor oxides and commercially available transparent electrodes were utilised. Monolayer coverage's were routinely obtained at these surfaces by soaking the support in a dilute solution of the complex of interest in a dry organic solvent. On the conductive supports, cyclic voltammetry was commonly used to probe the surface coverages of the

self assembled monolayers. The stability of the monolayers was monitored under continuous redox switching. In the present work, upwards of 20 carboxylic acid containing redox active molecules have been demonstrated to attach to the metal oxide supports with varying range of stabilities. The greatest stabilities (as determined from surface coverage's extracted from cyclic volyammetry) were observed when the electrochemistry was performed in non-hydrogen bonding solvents.

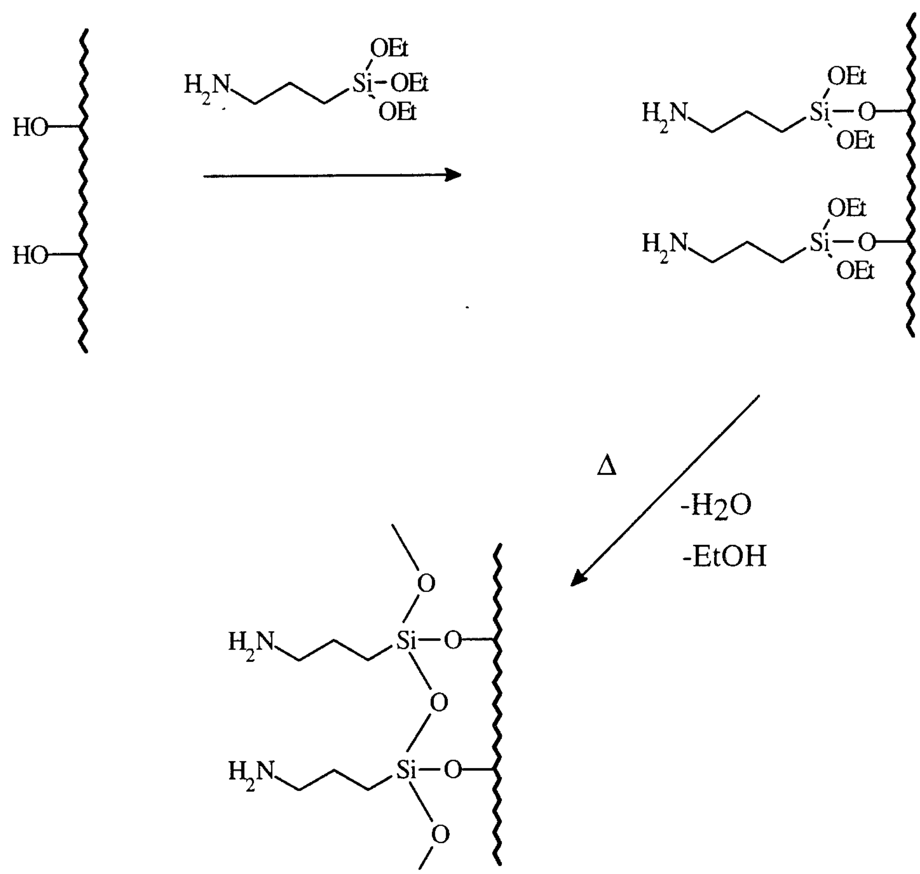
Of primary importance to this research was the determination of the nature of the surface linkage. This was probed by using resonance Raman spectroscopy on $Ru^{II}(bpy)_2(4,4'(COOH)_2bpy]^{2+}$ self assembled on SiO_2, powdered SnO_2 and TiO_2. It was elegantly demonstrated that the surface linkage on and powdered SnO_2 and TiO_2 constituted covalent ester linkages between the surface - OH groups and the acid groups on the bipyridine ligand. On SiO_2 two modes of interaction were observed - H-bonding interactions occurred between the bipyridine-COOH and either surface oxo groups or possibly surface bound water. This was the major mode of interaction. Minority ester formation was also shown to play a role.

The importance of hydrogen bonding type interactions was further confirmed with the observation that molecules that do not contain carboxylic acid functionalities had the ability to bind to the conductive metal oxide substrates of ITO and ATO. Examples included the alcohol functionalised complex $[(Os^{II}(bpy)_2(4\text{-}CH_2CH_2OH,4'\text{-}Me\text{-}bpy)]^{2+}$, where immobilization was proposed to occur via hydrogen-bonding interactions between the OH and surface oxo groups. $[Os^{II}(bpy)_2Cl(pz)]$, where pz=pyrazine, was found to form stable monolayers on In_2O_3 presumably through coordination of the N lone pair of the imine base.

In the course of this research we have explored in great detail, the factors affecting the formation of self assembled monolayers on metal oxide surfaces. This has been possible as a result of the large inventory of molecules that the group possesses, along with the synthetic capabilities of this group and the group of Bruce Ericksons at UNC. The observation that a wide variety of molecules containing different functional groups had the ability to self-assemble on the metal oxide supports is important. This demonstrates that more than one mode of attachment to the metal oxide supports is possible. The question of long term stability still remains. Greatest stability is observed in non hydrogen bonding solvents. Transferring the self assembled monolayers to water results in almost complete removal of the surface layer. This again emphasizes the importance of hydrogen bonding interactions in the self assembly process.

(B) Silyl Derivatized Monolayers on Semiconductor Electrodes

In the second approach ITO and ATO electrodes were chemically derivatized with 3-(aminopropyl)triethoxysilane (APS) forming a stable silane monolayer containing reactive amino groups. The research in this area was not as exhaustive as on the self assembled monolayers and as a consequence is still at a preliminary stage.



(Idealized Silane Monolayer)

The thickness of the resulting silane layer was measured by ellipsometry, and was found to be highly dependent upon the method used to deposit the silane layer. Close to monolayer coverages were obtained by using a vapor deposition technique. The semiconductor electrode was suspended above a solution of APS for a period of time. Polymerization of the adsorbed APS was induced by heating the electrode in an oven at

80°C. Redox active amino acids and peptides containing redox active groups were successfully coupled to the electrode via ester formation with the reactive amino group.

Electron transfer between the electrode and the attached redox active moiety was confirmed by cyclic voltammetry. A feature of the silyl derivatized electrodes is the enhanced stability of the monolayers in comparison to the self assembled interfaces. The possibility also exists for the molecular engineering of these interfaces based upon peptide coupling chemistry - an avenue being further explored in our laboratory in conjunction with the group of Professor Bruce Erickson.

Part 2: Electron Transfer and Excited State Properties of Self-Assembled Monolayers

Concurrent with the research on the nature of the self assembly process of complexes at the metal oxide surfaces, investigating the fundamental properties of the surface immobilized molecules was of paramount importance in this work. The redox properties of electroactive molecules at the semiconductor supports has been widely investigated for a variety of molecules. Cyclic voltammetry was the method of choice in detailing the redox properties. In general, the redox properties of the self-assembled monolayers on the semiconductor electrodes, paralleled those of the corresponding monomeric species in solution. Experiments were conducted in order to establish the potential of the oxide linkage chemistry for preparing surface assemblies in which more than one redox couple was bound. Stable mixed monolayers of $[Ru(bpy)_2(4,4'-(CO_2H)_2-bpy)]^{2+}$ and $[Ru(tpy)(4,4'-(CO_2H)_2-bpy)((H_2O)](PF_6)_2$ were prepared by competitive binding from the same solution. The redox response for each component was evident from cyclic voltammetry.

One of the expected advantages of immobilization was to hinder bimolecular interactions between surface bound molecular units. However, the existence of chemical interactions between species surface attached to ITO electrodes was clearly demonstrated. In solution, one electron oxidation of $[Ru^{II}(tpy)(bpy)(NO_2)]^{2+}$ produces $[Ru^{II}(tpy)(bpy)(ONO)]^{3+}$ which rapidly reacts with another $[Ru^{II}(tpy)(bpy)(NO)_2]^{2+}$ to produce $[Ru^{II}(tpy)(bpy)(ONO_2)]^{2+}$ and $[Ru^{II}(tpy)(bpy)(NO)]^{3+}$. The mechanism for this reaction pathway has been established in solution. Each of the molecular species has been identified by their distinct redox potentials. Parallel reactivity occurs with the surface attached $[Ru^{II}(tpy)(4,4'-COOH)_2-bpy)(NO_2)]^{2+}$ species. The electrochemical evidence

supports the occurrence of bimolecular chemistry. This can only occur if adjacent molecular units are mobile and/or flexible enough to assume geometries suitable for bimolecular reactivity. This is a revealing observation. It clearly demonstrates 2-dimensional intermolecular reactivity - a property which may be exploited for potential device applications.

Much greater perturbations on the excited state properties of the surface confined species were observed in comparison to the well established solution based studies. Emission studies and excited state lifetimes were determined for the surface-oxide bound chromophores. The excited state properties of the polypyridyl complexes were highly dependent upon support type and loading. Emission decay of the metal-to-ligand charge transfer (MLCT) excited state of $[Ru^{II}(bpy)_2(4,4'-(COOH)_2bpy)]^{2+}$ attached to glass slides was found to be nonexponential with average lifetimes ($< \tau >$) from < 5 ns to 600 ns with CH_2Cl_2 in the external solution. The average lifetime was found to increase at lower surface coverages. The photophysical data give strong evidence for excited-state ground-state interactions. On powdered silica monoexponential behavior was observed for the emission decay of the MLCT excited state. This is a result of the much lower surface coverages (10^{-13} moles/cm^2). On the semiconductor supports, lifetimes of the MLCT excited state for the Ru(II) emitters were < 5 ns as a result of rapid quenching of the MLCT excited state by the electrode.

Assemblies of $[Ru^{II}(bpy)_2(4,4'-(COOH)_2bpy)]^{2+}$ were prepared on insulating glass slides with coattached quenchers based on carboxylic acid containing viologens, phenothiazines, or $[Os^{II}(bpy)_2(4,4'-COOH)_2-bpy)](PF_6)_2$ by competitive binding. Quenching of the MLCT excited state of the Ru(II) emitter by electron or energy transfer was observed by transient spectroscopic techniques. The demonstration of lateral electron and energy transfer across the surface of the metal oxide supports is a significant observation.

The perturbations on the excited state properties of surface oxide bound emitters are significant. The photophysical properties for the excited states of the suraface bound species are expected to be strongly influenced by the immediate environment of the bound complex. As a consequence, such studies provide valuable insight to the nature and integrity of the self-assembled complexes. The demonstration of 2-dimensional reactivity - as confirmed by the redox chemistry of $[Ru^{II}(tpy)(4,4'-COOH)_2-bpy)(NO_2)]^+$ and from the observation of lateral electron and energy transfer across non conducting supports lends credence to the possibility of using such interfaces for device applications.

Part 3 : Sol-Gel Chemistry

In the last of the interim technical reports, details were given on a new avenue of research being explored in this laboratory, namely that of the immobilization of ruthenium polypyridyl complexes in silica gel monoliths. These optically transparent silica monoliths are prepared by the controlled hydrolysis and condensation of tetramethoxysilane (TMOS). The final free standing gel is prepared at room temperature. The ruthenium polypyridyl complex is included in the water/methanol/formamide/TMOS mixture from which the gel is manufactured. Glass gels were molded from polystyrene cuvettes and the final gels usually have dimensions of 1.5 cm x 0.5 cm x 0.5 cm. The complex becomes immobilized in the polymerizing SiO_2 network as hydrolysis and condensation of the TMOS occurs.

Although the interest in this chemistry stems directly from the previously described work, it should be noted that it is not necessary for the immobilized molecules to contain groups capable of interacting with the SiO_2 network. Immobilization occurs by both strong electrostatic interactions and also by physical entrapment within the polymerized SiO_2 network. The optically clear nature of the gels allow for characterization of the immobilized molecules by conventional spectroscopic techniques including visible absorption. The gels can also be immersed in a variety of solvents.

To date the study has focused on two areas. The photophysical properties of $[Ru(bpy)_3]^{2+}$ and related polypyridyl complexes have been studied in detail. In addition, a series of donor-chromophore-acceptor assemblies of the type *trans*-$[Ru^{II}(bpy)_2(D)(A)]$ where a typical acceptor (A) is (N-methyl-4,4'-bipyridinium) and a typical donor (D) is (10-(4-picolyl)phenothiazine). In solution, photoinduced isomerization and ligand loss are facile at room temperature. Much greater stability is observed for the sol-gel immobilized species. This enhanced stability has also been observed for other photochemically unstable species. Sol-gel immobilization represents a novel method of influencing the excited state properties. The attenuation of the excited state properties of ruthenium polypyridyl complexes has also been demonstrated for other complexes. In aqueous solution at room temperature $[Ru^{II}(bpy)(tpy)(NH_3)]^{2+}$ has an excited state lifetime of < 10 ns. For the sol-gel immobilized species, immersed in water, the MLCT emission decay shows nonexponential behavior with an average lifetime > 100 ns.

The catalytic oxidation chemistry of $[Ru^{II}(bpy)(tpy)(OH_2)]^{2+}$ has been explored for the sol-gel immobilized species. Visible absorption spectra confirm the formation of the $Ru^{IV}{=}O^{2+}$oxidant upon introduction of hypochlorite to the gel immersed in water. This species was able to affect the oxidation of various organic reagents. The ability to

monitor this catalytic cycle by visible absorption is a great advantage. It has been shown that $[Ru^{II}(bpy)(tpy)(OH_2)]^{2+}$ exists in the matrix in two distinct environments. As well as *normal* $[Ru^{II}(bpy)(tpy)(OH_2)]^{2+}$, a species which interacts strongly with the SiO_2 matrix is present. This is confirmed by immersing the gel in acetonitrile solution. Approximately 60% of ruthenium bound aqua groups are replaced by the stronger binding acetonitrile ligand. The second species is proposed to be bonded Ru-O-Si in which it is not possible for acetonitrile to bind. This silica bonded complex has an absorption maxima at 500 nm. This was clearly distinguishable from the acetonitrile complex. Emission also occurs from the proposed bound species at 720 nm confirming the existence of a second distinct complex.

These observations are important. Immobilization of such catalysts at solid supports continues to be widely investigated and spectroscopic information is valuable in determining the nature and integrity of the immobilized molecules.

Conclusion

Work in the areas described above is currently ongoing as part of a further ARO funded research grant. The extensive work to date has provided a wealth of information on the formation and properties of monolayer derivatized metal oxide supports and on the immobilization of complexes at silica sol-gels. The present research effort is being directed towards building, at the metal oxide supports, more complex molecular assemblies with well defined redox and photophysical properties.